The Determining Role of Abiotic CAH Fate Processes:

Possible Impacts on Your Remedy Plans and Implementation Efforts

Leigh Alvarado Benson
Parsons Corporation
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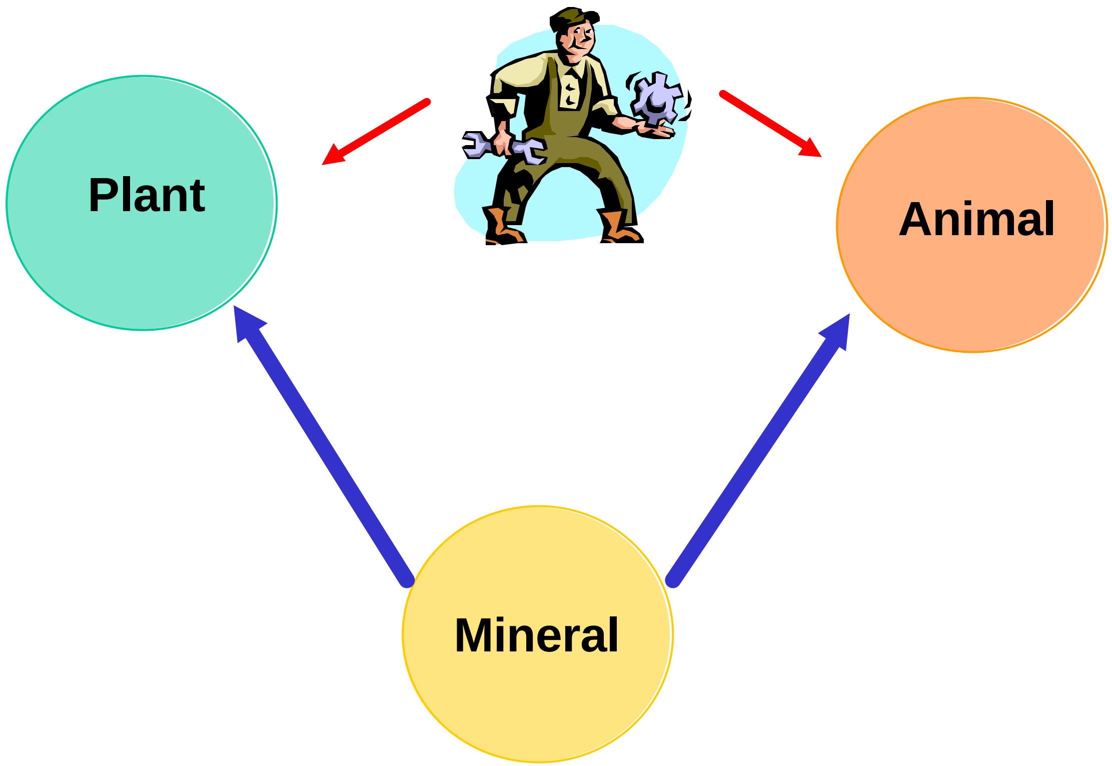
Guiding Questions

- **Is microbial degradation the only means of achieving *in-situ* CAH degradation in a reasonable timeframe?**
- **What, typically, is overlooked when designing these types of remedies? (Hint: the determining role of abiotic reactions in the fate of CAHs)**
- **What might that science/design flaw be costing you?**
- **How can you develop better *in-situ* CAH remediation strategies that exploit both biotic (rapid) and abiotic (sustainable) elements?**

Soil Composition Effects



Primary control on the diversity and metabolism of plants & animals is the nature of carbon and energy sources.

What controls the nature of carbon and energy sources?

(Hint: Both right answers begin with the letter "M")

Soil Microbial Ecology

- *In-situ* CAH treatment potential depends on:
  - Contaminant properties
  - Soil/groundwater geochemistry
  - Microbial community properties
  - Duration of ecosystem exposure (residence time/aging effects)

- Microorganisms accumulate at soil particle surfaces where potential energy sources and nutrients are concentrated
  - Greater availability of energy sources and nutrients at the soil particle surface than in the aqueous phase
  - Successful microbial growth dependent upon forming and sustaining structured surface colonies (biofilms)
  - Microbial communities attached to particle surfaces survive longer, grow faster, and degrade CAHs more quickly than non-attached microbes(i.e., those transported in the aqueous phase)

CAH Fate Controls

- Processes controlling the environmental fate of CAHs
  - Volatilization
  - Leaching and mass transport processes
  - Adsorption/desorption and sequestration within the soil matrix
  - Plant uptake
  - Abiotic transformations
  - Biodegradation
- All processes co-exist and all contribute to long-term CAH concentration, mass, toxicity, mobility, and persistence
- Soils (unsaturated/saturated) = complex, catalytic systems
  - Biotic catalysts (bacteria, fungi, algae, enzymes, viruses, other biota)
  - Abiotic catalysts (organic matter, oxides, hydroxides, clays)
- Biodegradation believed to be the *primary* force in CAH transformation, based on extensive lab work on microbial metabolic activity → enhanced remediation strategies

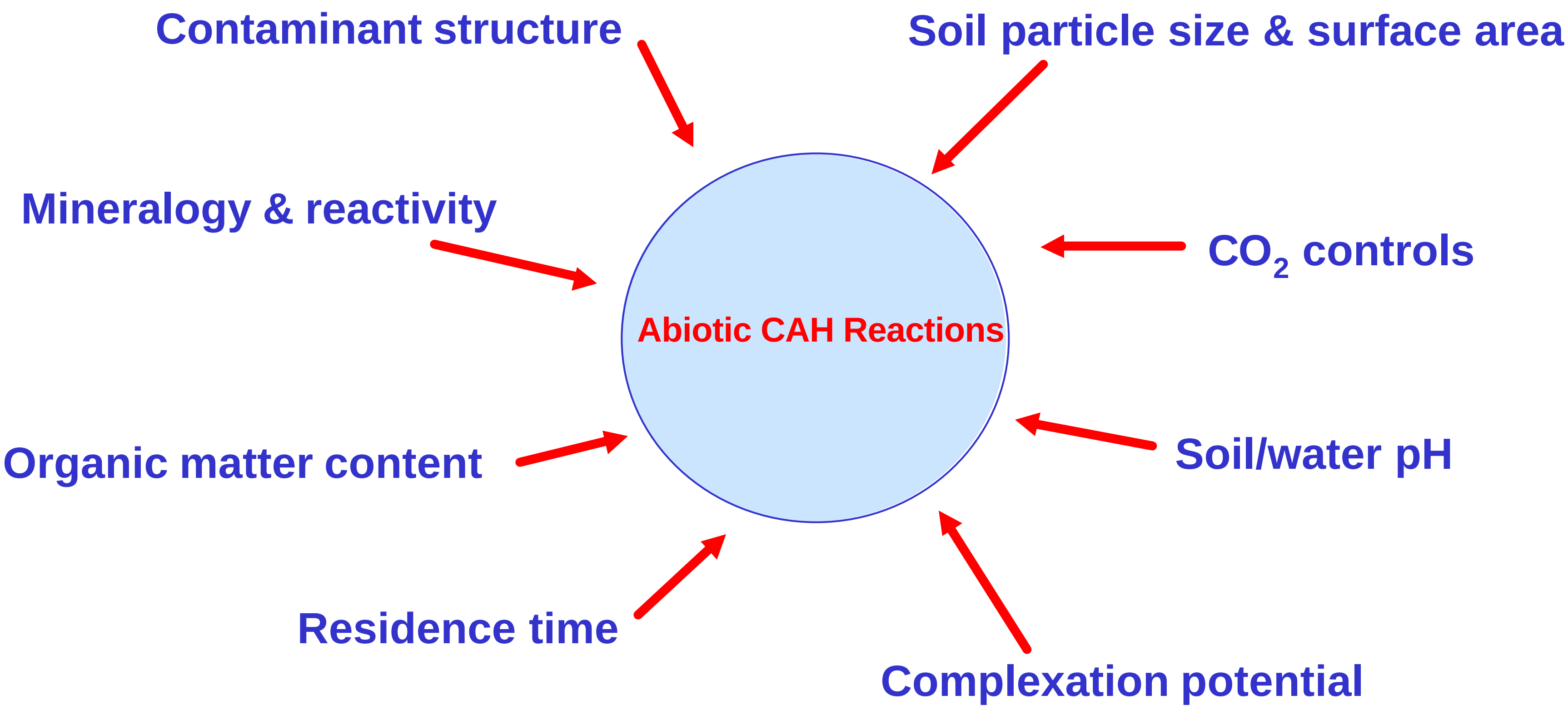
But in the Environment…

- **Laboratory conditions (simple) $\not\approx$ Natural systems (complex)**
- **Natural system disrupted by CAH release (reaction catalyst); natural reactions occur toward restoring equilibrium**
  - **Mineral precipitation/dissolution reactions (weathering)**
  - **Complexation and adsorption**
  - **Oxidation/reduction reactions**
- **Biotic catalysts are a *subset* of these natural reactions**
  - **Easier to anthropogenically manipulate (enhance by engineering)**
  - **Kinetically more rapid under right conditions (easier to "see" quickly)**
  - **Hard to sustain without continued intervention**
  - **Must account for the "natural order" of the system**
- ***Abiotic catalysts will dominate* these natural reactions**
  - **Will be important at time scale of environmental transport**
  - **Sustainable (as long as we do not further "muddy the waters")**

Substrate Availability

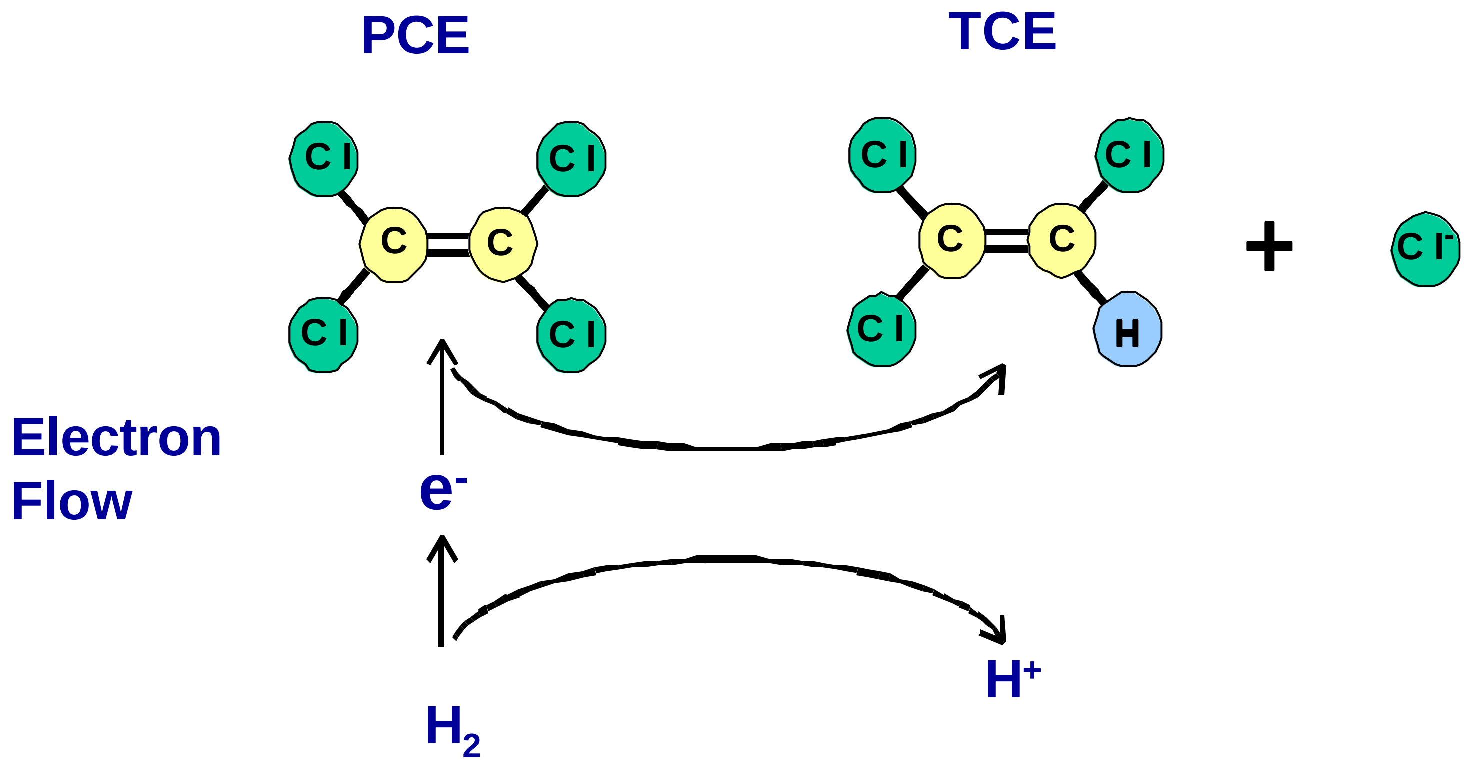
- **Sustaining CAH degradation depends on sustaining substrate accessibility**
  - **Engineered enhanced biodegradation systems depend on sustaining microbial communities and sufficient bioavailable reactants**
  - **Environmental changes effected by both biotic and abiotic processes may reduce biodegradation potential over time**
- **Soil particle surfaces:**
  - **Support effective microbial communities**
  - **Provide infinite mass of reactants for biotic degradation reactions**
  - **Abiotically transform CAHs until equilibria are restored**

Abiotic Transformations



Abiotic Catalysis of CAHs

Adsorbs to soil particle surfaces ⏩ chemical reaction ⏩ release of byproducts

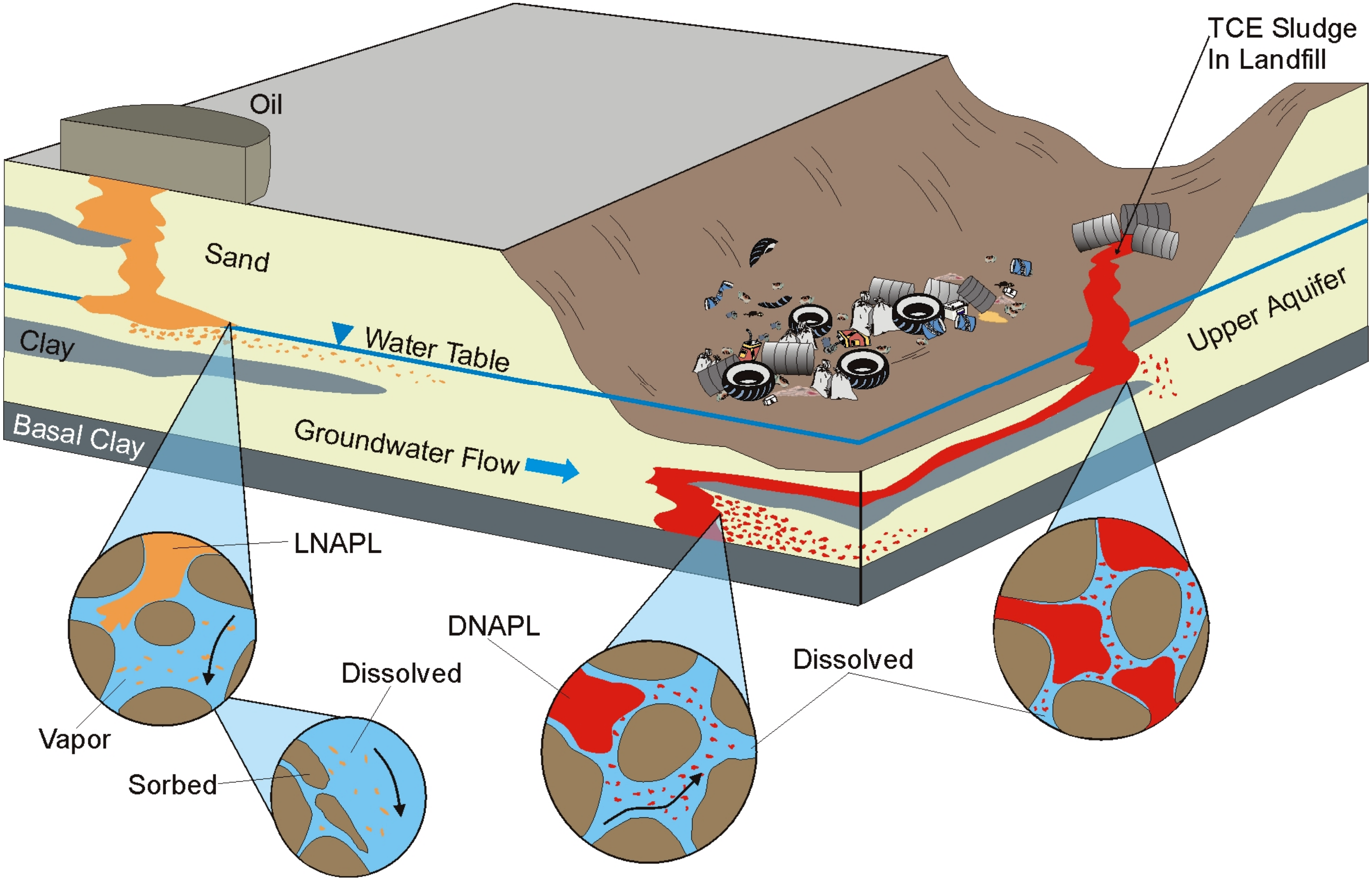


Facilitated soil weathering ⏩ chemical reaction ⏩ release of byproducts

Mineral Facilitators

- Inorganic components
  - Kaolinites and bentonites
  - Montmorillonites
  - Clay minerals, especially Fe(III) and Cu(II) smectites
  - Al, Fe, Mn, and Ti oxides
- Abiotic reactions ⇦⇨ Biotic reactions
  - Probability of bioavailability decreases with age
  - Phasing engineered enhanced biodegradation remedial systems over space and time
- Realized degradation rates/capacity may be controlled by complex mass-transfer and chemical rate kinetics
  - Sequestering *vs*. soil dissolution
  - Bioavailability *vs*. inorganic transformation

Case Study: DSCR CAH Plume



P&T Effect on CAH

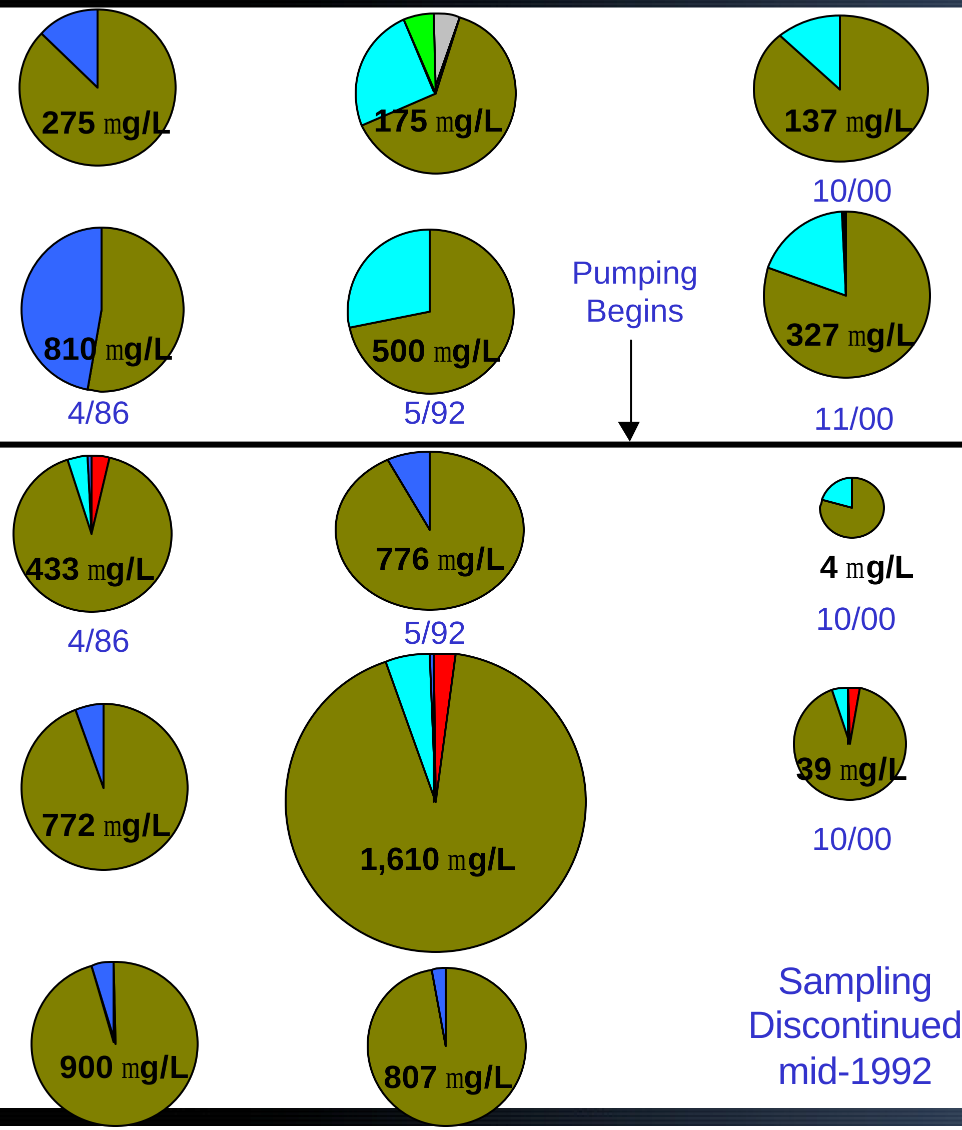
USGS-B5
(Upper WBU)

USGS-B4
(Upper WBU)

USGS-B3
(Lower WBU)

USGS-B2
(Lower WBU)

USGS-B1
(Lower WBU)



No appreciable mass change, containment not effective

Chemical evolution observed, basis for transformation?

pH < 4.5 (Biotically hostile!)

Effective but not complete mass containment

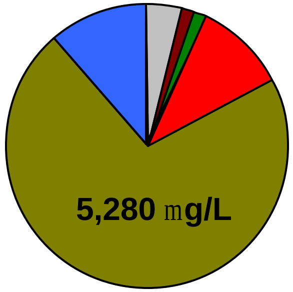
Some chemical evolution observed, basis for transformation?

pH < 5 (Biotically hostile!)

DSCR "Unexpected" Groundwater Quality Data

AEHA-28A
(Upper WBU)

pH < 4.5
(Biotically hostile!)



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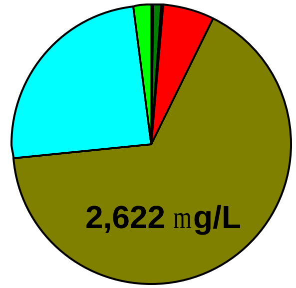

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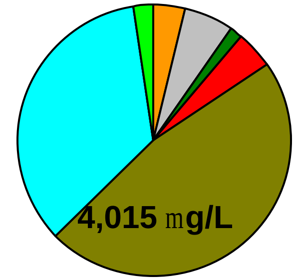

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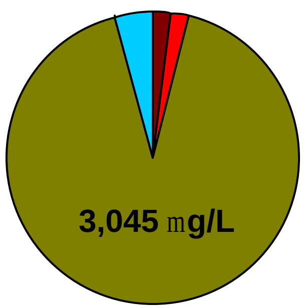
Slow conversion from PCE → TCE → DCE → VC

Upper well not significantly affected by pumping (hydraulic constraints), see evidence of "DCE stall"

Lower well affected to some degree by pumping

AEHA-28B
(Lower)

pH < 5
(Biotically hostile!)



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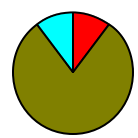

10 mg/L

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Not Detected

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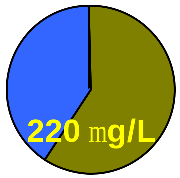
DSCR More “Unusual” Data

AEHA-27A
(Upper WBU)

pH < 6
(Biotically unfavorable!)



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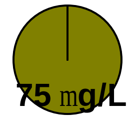

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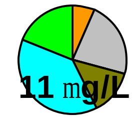


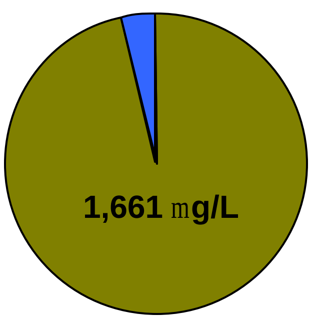
10/00

Slow conversion from TCE → DCE → VC

Upper well not significantly affected by pumping (hydraulic constraints), lower well affected to some degree by pumping

AEHA-27B
(Lower WBU)

pH < 6
(Biotically unfavorable!)



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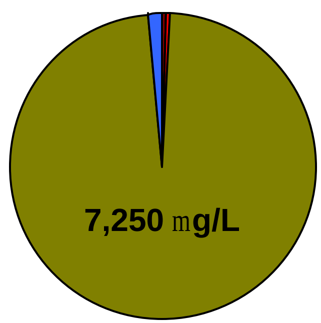

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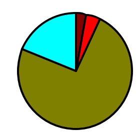

30 mg/L

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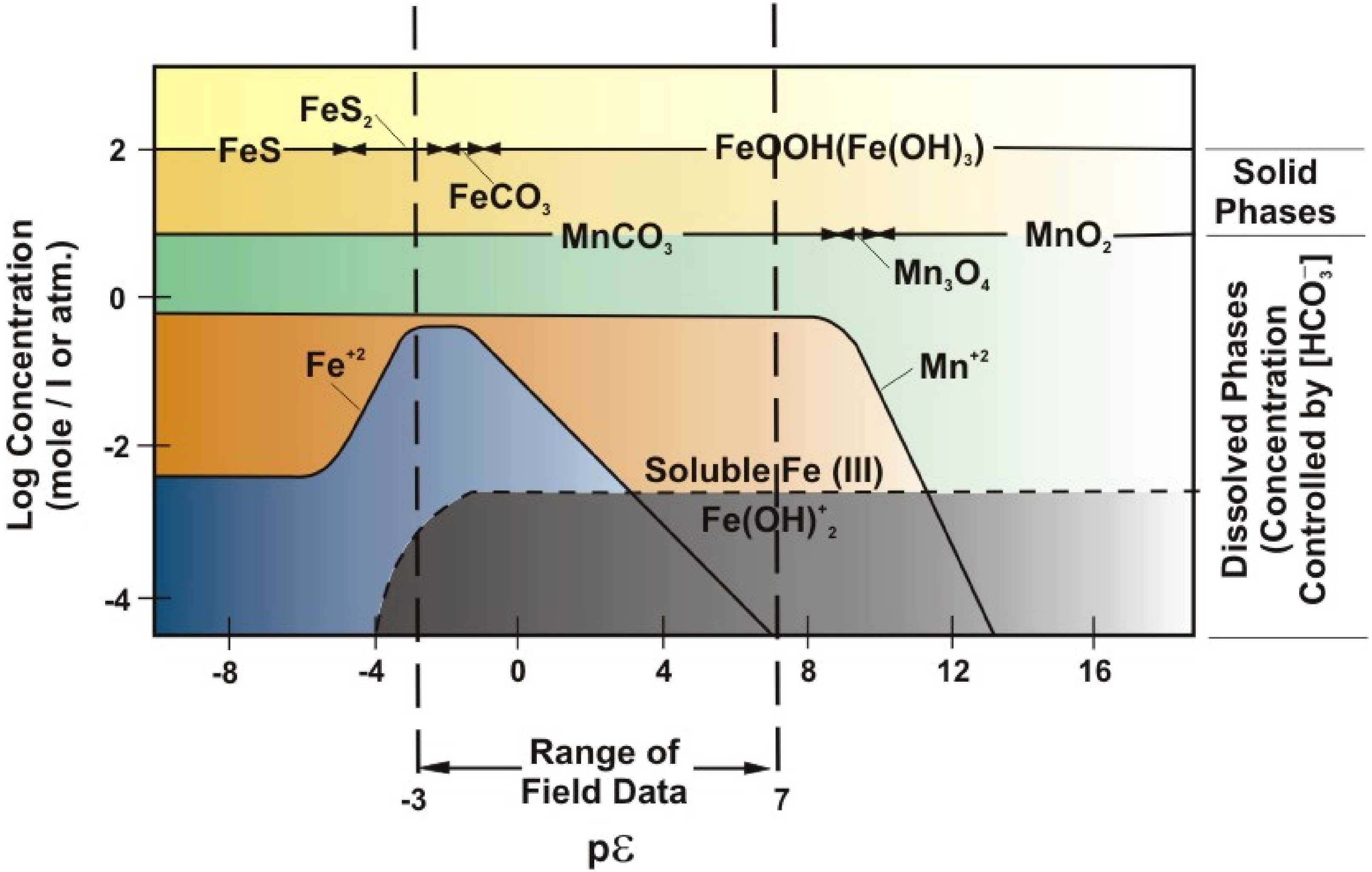
Solving the CSM Puzzle

- **P&T system is being adversely affected by some type of biogeochemical fouling**
  - **On-site “liquid” iron conditions (100s ppm)**
  - **Other redox-sensitive metals elevated on-site (Al, As, Cu, Mn, Zn) – complexed?**
  - **Elevated “common” inorganic components (e.g., Ca, Mg, K)**
  - **Low buffering capacity, low pH**
  - **Low reported organic content (old landfill)**
  - **Where are these metals coming from?**

Iron at pH Less Than 5



DSCR Weathering Model

Feldspar	→	Chlorite	→	Illite	→	Kaolinite
$3\ KAlSi_3\ O_{8(s)}$		$(Mg, Al)_{12}[(Si,Al)_8O_{20}](OH)_{16}$		$K_xAl_4(Si_{1-x}Al_xO_{20})(OH)_4$		$Al_4(Si_4O_{10})(OH)_8$

- Presence of FeO affects weathering of granite
- Weathering similar to hydrolysis, partial exchange of Si for OH^-
- Weathering rate usually slow

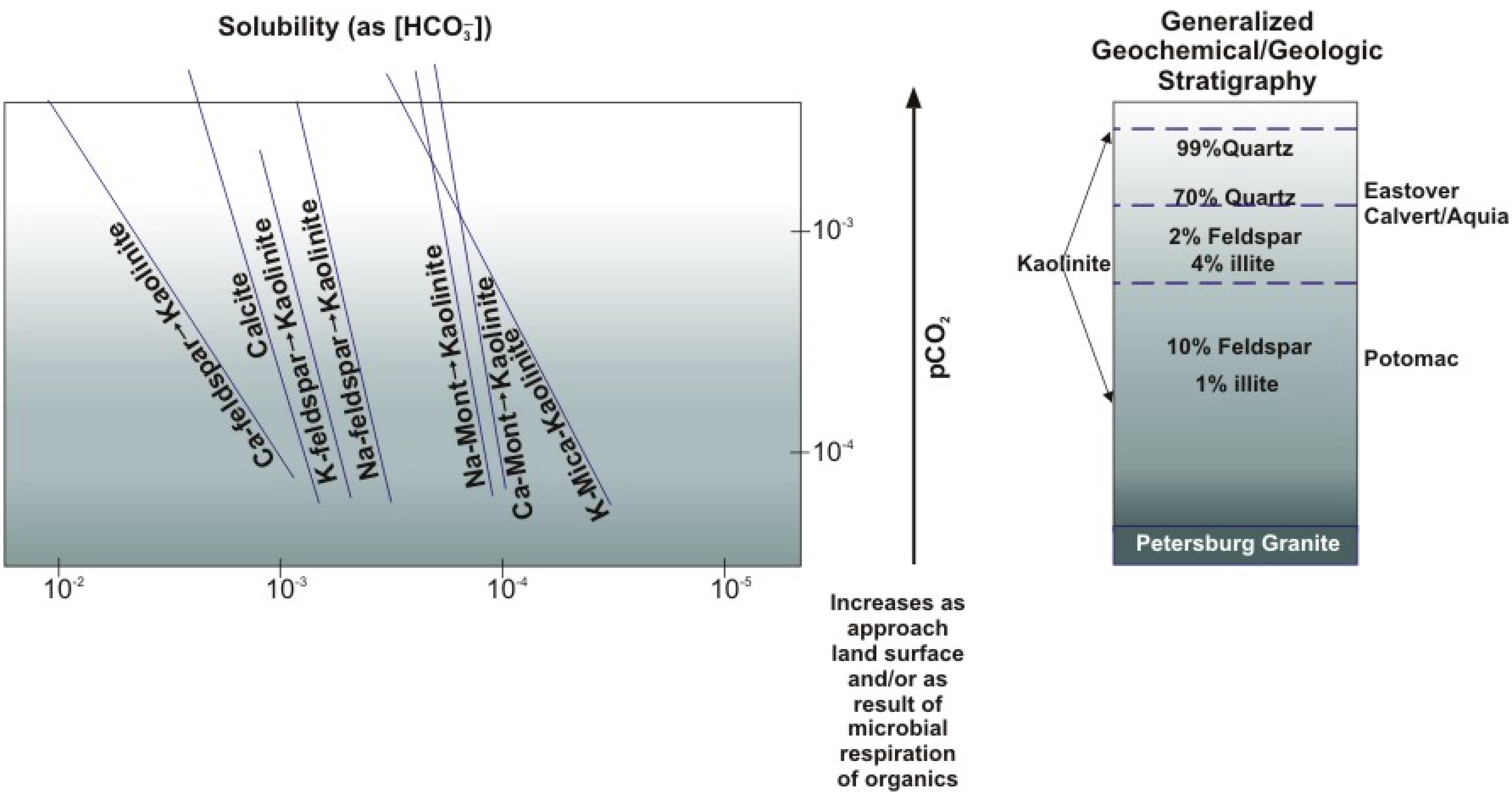
Unless

Redox process produces OH^- which can "leach" specific rock constituents (Al, Ca, Fe, Mg, K)

Organic matter (natural/anthropogenic), including LMW organic acids, act as chelate complexers

Speeds weathering mobilizes metals, affects groundwater chemistry

Mineral Weathering at DSCR



Considering Abiotic Processes in Remedy Designs

- **Age of CAH release?**
- **Source of elevated metals?**
- **Field conditions suitable for biological primacy?**
- **Mineralogical characteristics consistent with abiotic transformation?**
- **Intervention potential best applied where and when?**
- **What are your performance criteria for an engineered enhanced bioremediation remedy when phased in context with natural abiotic transformations?**
- **Should you intervene at all?**

We Know Not What We Do

- **Is our intervention compromising other CAH transformation processes, and slowing the natural recovery potential of any site? $$$$$$$**
  - **Does adding any energy source change the characteristics of soil surfaces and surrounding water quality that control microbial communities and abiotic transformations?**
  - **Does enhanced biological activity change soil surfaces (e.g., enzymatic activity) to slow or terminate other CAH transformation processes?**
- **Are we considering the importance of ageing on the availability of CAHs to engineered techniques? $$$$$$$**
  - **Bioavailability decreases with time**
  - **“Bound” CAHs may be subject to abiotic reactions**
- **Are we recognizing the potential for and significance of different processes that control CAHs as a function of depth?**
  - **Biodegradation may be important in near-surface media**
  - **Abiotic reactions will dominant in deeper, un-weathered strata**

So Now What?!

- Is this "bad news" for enhanced bioremediation remedial strategies? **No – well, sorta**
- Engineered system RD/OMM&M must account for the full range of soil mineral-organic matter-microbial interactions
  - Expedited weathering in source areas may provide required reactants for biotic and abiotic transformations
  - Enhanced engineered systems have a specific application in phased groundwater remediation plans
  - Carefully consider mineralogy and resultant natural water quality controls before enhancing any subset
  - Review available site data to refine remedy performance objectives

Screening for Abiotic Reactions

- **Review your site data for evidence of controlling abiotic transformation processes**
  - **Compatible mineralogy**
  - **pH, dissolved inorganics, CO_2**
  - **Common anions and cations**
  - **Turbidity, TSS**
  - **Groundwater quality analysis (e.g., geochemical controls evaluation)**
  - **Background characterization results**
- **Consider collecting the following "specialized" data as part of remedy planning/design**
  - **Soil mineralogy by thin-section & XRD**
  - **Mineral dissolution potential**
  - **Extractable oxides**
  - **Soil precipitates and surface area analysis**

Answers to Guiding Questions

- **Is microbial degradation the only means of achieving *in-situ* CAH degradation in a reasonable timeframe?**

  No – abiotic degradation may provide long-term control

- **What, typically, is overlooked when designing these types of remedies?**

  The importance and significance of soil particle surfaces in controlling CAH degradation potential

- **What might that science/design flaw be costing you?**

  We cannot fight Mother Nature at any reasonable cost

- **How can you develop better *in-situ* CAH remediation strategies that exploit both biotic (rapid) and abiotic (sustainable) elements?**

  Phase your response in time and space